

Alkali Sorption in Second-Generation Pressurized Fluidized-Bed Combustion

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Modern second-generation pressurized fluidized-bed combustion (2nd-Gen. PFBC) combined cycle power systems are developed to increase the efficiency of coal combustion. However, combined cycle power systems require reliable hot gas cleaning. The alkali metals sodium and potassium can lead to severe damage of the gas turbine blades, because of hot corrosion. This investigation was conducted to assess the potential for the reduction of alkali metals from hot gas by different aluminosilicate sorbents, such as silica, bauxite, bentonite, and mullite, under reducing atmospheres at a temperature of 750 °C. Using a flow channel reactor, an alkali chloride-laden gas stream was passed through a bed of aluminosilicate sorbents. Qualitative and quantitative analysis of the hot gas downstream of the sorbent bed was performed using high-pressure mass spectrometry (HPMS). Thus, the influence of different gas atmospheres on the alkali sorption was determined and conclusions were drawn concerning the chemical reactions that were occurring inside the sorbent bed. Moreover, annealing experiments were performed to determine the sorption capacity of the sorbent. Subsequent scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) and X-ray diffraction (XRD) analyses showed that the phases formed inside the tested sorbent materials. Sorbent capacities for sodium and potassium of up to 110 mg/g have been achieved after 192 h for bentonite. Finally, thermodynamic computations were performed to scale the results of the laboratory experiments up to the conditions prevalent in 2nd-Gen. PFBC systems. The investigations revealed the possibility of reducing the overall alkali concentration in the hot gas under 2nd-Gen. PFBC conditions to values of <50 ppbv through the use of bentonite and activated bauxite. The amount of sorbent needed for a 500 MW_{el} power plant was estimated to be ~100 kg/h at a hot gas temperature of 700 °C.

Introduction

Economic and environmental considerations require an increase of the efficiency of coal-fired power plants. In ordinary pressurized fluidized-bed combustion (PFBC), the combustion temperature is limited to values of <900 °C, to prevent slagging inside the combustion chamber. The demand for higher efficiencies and, therefore, the need for higher combustion temperatures has led to the development of a second-generation pressurized fluidized-bed combustion (2nd-Gen. PFBC) combined cycle system (Figure 1). This system mainly consists of a two-stage combustion operating at a pressure of 10–16 bar. In the first stage, the coal is gasified under reducing conditions (air/fuel ratio of $\lambda < 1$) at temperatures of 650–750 °C. Coal contains small amounts of sodium and potassium in different chemical forms, such as salts or clay minerals; these alkali metals are partly released during the gasification process and can cause high-temperature corrosion of turbine blades at operating temperatures of >600 °C. Therefore, after leaving the first stage, the flue gases pass a gas-cleaning section, which consists of ceramic filters for ash removal and

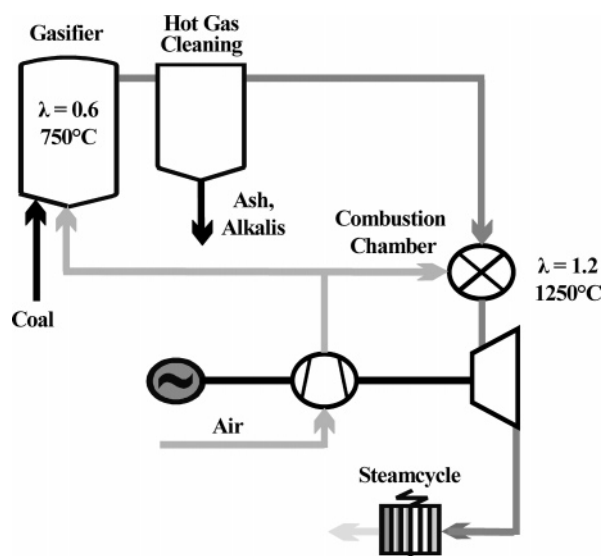


Figure 1. Schematic flow diagram of the second-generation pressurized fluidized-bed combustion (PFBC) combined cycle process.

an alkali sorption unit. The cleaned gas is then mixed with a secondary air stream and either burned in a second combustion chamber or directly inside the gas

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turbine, in both cases at $\lambda > 1$. The residual thermal energy of the gas stream leaving the turbine is finally transferred to a steam cycle. The 2nd-Gen. PFBC has two main advantages over an ordinary PFBC system: (i) as a result of the two-stage combustion, the gas turbine entrance temperature can be raised to 1250 °C, which leads to an increase in the total efficiency of the system, and (ii) the positioning of the gas-cleaning section into a region of low temperature offers good possibilities for improved ash and alkali removal. The maximum amount of gas-phase sodium and potassium species in the flue gas entering the gas turbine should be <50 parts per billion, by weight (ppbw).^{1,2}

The most preferable method of alkali control is to pass the combustion gases through a fixed bed of inorganic solid sorbents.³ Possible sorbents should show high-temperature stability, fast sorption kinetics, and high loading capacity.¹ Thermodynamic calculations and earlier investigations by other authors have revealed aluminosilicates as suitable sorbent materials to fulfill this task.^{4,5}

Most of the past investigations on alkali removal were concerned with cleaning high-temperature (800–900 °C) flue gases from ordinary PFBCs.^{6,7} For this reason, the major part of the past research focused on removing alkali species, such as chlorides and sulfates, from simulated flue gases (SFGs) under oxidizing conditions.⁵

Other than thermogravimetric investigations, the packed-bed method was the most favored experimental approach.^{6,8–10} The latter one was the only method to provide data concerning the degree of purification of a gas stream from alkali species. The packed-bed method was used to examine the influence of superficial gas velocity and gas hourly space velocity, carrier gas composition and moisture content, sorbent bed temperature, pressure, and elapsed time.^{7,10} In most cases, a solid source of alkali chloride was used. An overview of the investigations concerning alkali sorption has been given by Wolf.¹¹

In packed-bed methods, the alkali capture was determined either by monitoring the alkali content of the gas exiting the packed bed or by analyzing the sorption material after completion of the test. Determining the alkali content of the gas downstream of the sorbent bed has been, in most cases, done by quenching the gas stream after the sorbent bed and analyzing the condensate for alkalis via atomic absorption spectroscopy (for potassium) or atomic emission spectroscopy (for sodium).^{7,12–15} In contrast to this batch sampling technique, several on-line methods for alkali quantification have been developed. Among others, flame atomic emission spectroscopy (FAES)^{2,16–19} and plasma-excited alkali resonance line (PEARL) spectroscopy have been used in most of the experiments.²⁰ Using these methods, sodium and potassium levels in the ppbv to ppmv (parts per million, by weight and volume, respectively) range have been determined.

The best performing sorbents under oxidizing conditions were activated bauxite, emathlite, and kaolinite.⁵ The sorption mechanism was shown to be strongly dependent on the silica content of the sorbent. For sorbents with high silica content, the chemical reaction of the alkali with the lattice of the sorbent was predominant. For activated bauxite, both chemical and physical sorption were reported.^{7,12}

The influence of the reducing atmosphere on alkali removal by solid sorbents has been investigated to a much lower extent. Experiments in reducing atmospheres were either conducted at high temperatures of 850–900 °C using mixtures of N₂/H₂ or simulated flue gases, in respect to coal gasification systems,²¹ or for the control of alkali species in biomass gasification

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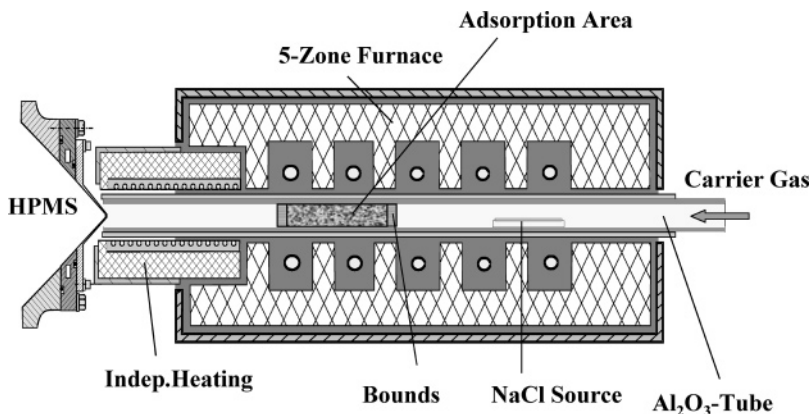


Figure 2. Schematic representation of the high-temperature reactor used for the alkali sorption experiments.

systems at temperatures of 660–725 °C.²² In the latter investigation, biomass gasifier gas was used, which makes evaluation of the results difficult.

Laboratory experiments of alkali uptake by aluminosilicate sorbents in a reducing environment at 750 °C have not been performed so far. Data on sorption kinetics and the rate of alkali uptake must be determined. The sorption mechanism responsible for alkali uptake is of great concern and must be determined under these conditions. The aim of this work is to determine (i) the influence of different sorption materials, (ii) the influence of water on the alkali uptake under reducing conditions, (iii) the influence of sulfur on the sorption process, (iv) the influence of sorbent bed length, and (v) the maximum reduction of alkali concentration that can be achieved.

None of the methods used in the literature for gas-phase alkali analysis so far could provide simultaneous on-line measurement and determination of the alkali species in the gas. For this reason, during the alkali sorption experiments described in the literature, no conclusions about the ongoing chemical reactions inside the sorbent bed could be made.

Considering these aspects, a new method must be used; this method must be able to deliver both quantitative and qualitative analyses. This work describes the first approach to using high-pressure mass spectrometry (HPMS) for the analysis of alkali species in packed-bed studies and for the investigation of the sorption behavior of different aluminosilicate sorbents.

Experimental Section

Tube Flow Reactor. All alkali sorption experiments presented in this work were performed as packed-bed studies. The setup mainly consisted of a heated-flow channel housed in a furnace with six independent heating zones (Figure 2). For the channel, a high-density alumina tube was used to prevent reaction of the tube walls with the gas-phase alkali species. Depending on the type of experiment, the inner diameter of the tube varied over a range of 20–25 mm, and the total length of the tube was 850 mm. The sorbent bed could be varied in length, from 10 mm to 150 mm, and was inserted into the tube between two Al₂O₃ plates drilled with several holes (diameter of 1 mm), to enable the gas stream to pass through them. The alkali source (NaCl) was positioned 15 cm

upstream of the sorbent bed at ~700 °C and consisted of a high-density Al₂O₃ crucible that contained 10 g of NaCl and had a surface area of 10 cm². For all experiments, a basic mixture of 3 or 4 L/min of He/H₂/H₂O was used. Helium was selected as the carrier gas, because its low atomic mass gave the highest signal intensities in the HPMS.

The gas stream was directed through a nebulizer, to provide the required moisture levels. Because of the six available independent heating zones of the furnace, all parts of the reactor downstream of the alkali source were kept at a higher temperature, relative to the source temperature. This prevented the alkali species from condensing on the tube walls downstream from the source. The last heating zone (150 mm) inside the furnace was kept at a constant temperature of 850 °C, because of the expected heat-transfer-induced decrease in temperature toward the flow channel exit. However, the hydrogen in the gas stream led to a flame formed by the reaction of H₂ with O₂ from the ambient air at the reactor outlet, which kept the tube walls at the flow channel exit at temperatures of >750 °C, making it impossible for alkali species to condense in this region. For the determination of the gas composition of the cleaned gas leaving the sorbent bed, this flow channel reactor was coupled to a HPMS system.

High-Pressure Mass Spectrometry System. HPMS is a highly suitable method that is used for hot gas analysis in the range from room temperature to 1500 °C at atmospheric pressure. The HPMS technique can deliver real-time, on-line analysis and specification of alkali-metal vapors. For this reason, the HPMS technique is ideally suited for determining alkali species downstream of a sorbent bed. The integrity of the sampled high-temperature, alkali-laden gases is preserved during the free-jet expansion, because chemical reactions are effectively quenched and condensation is inhibited. The non-equilibrium nature of the free-jet expansion and the subsequent formation of a molecular beam allows reactive and condensable species to remain in the gas phase at temperatures far below their condensation point for long periods of time, in comparison to reaction rates.²³ Using the mass spectrometer, comprehensive detection of all gas-phase species can be achieved with high sensitivity. The general setup for a HPMS system has been described in the literature; therefore, only additional information concerning the HPMS used in this study is given.²⁴ Recipient and major components of this HPMS have been self-constructed by Forschungszentrum Jülich GmbH.

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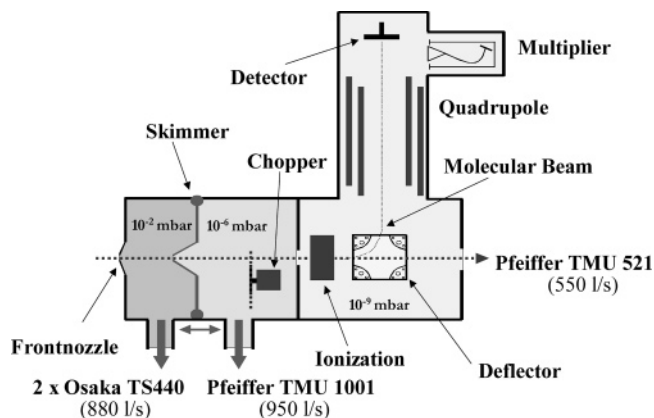


Figure 3. Schematic representation of the high-pressure mass spectrometer system.

A stainless-steel cone, 35 mm high with an interior angle of 108° and an orifice diameter of 0.3 mm was used for molecular beam sampling. This cone was fitted to a water-cooled stainless-steel flange that was connecting the HPMS recipient and cone. This front orifice cone was connected to the flow channel tube by moving the furnace toward the HPMS and sealing the small circular gap between the tube and cone with high-temperature insulation. The theoretical gas flow through the orifice at a given temperature and gas composition was calculated,²⁵ and the flow reactor was operated with some excess gas flow, to prevent ambient air from entering the gas stream. The protrusion of the orifice into the flow reactor prevented condensation on the sampling cone. Measurements at the tip of the cone revealed a temperature of 700°C at this region.

The HPMS system consists of a three-stage differentially pumped vacuum system (Figure 3). Pressures of 10^{-2} mbar for stage 1, 10^{-6} mbar for stage 2, and 10^{-9} mbar for stage 3 can be achieved during the measurements.

Sampled gases entering the system undergo a free-jet expansion. The core of the expanded gases is extracted by a conical skimmer (diameter of 1 mm) at the entrance of stage 2, forming a molecular beam. The skimmer is constructed to be moveable along the recipient's main axis from the outside during a running experiment. This way, the optimum skimmer position, depending on the sampled gases, can be found and the beam performance and the resulting signal intensity can be maximized. A shutter positioned upstream from the stage 3 entrance is installed to have the possibility of blocking the beam, for background scanning. The molecular beam enters the ionization region inside stage 3 by passing through another small aperture (diameter of 1.5 mm). Ions are formed by electron impact ionization. The ionization energy for the sorption experiments was 30 eV. The ions are filtered with a quadrupole analyzer (ABB Extrel)²⁶ and detected with an off-axis Channeltron electron multiplier. Control of the scanning parameters and collection of the multiplier signal, as a function of time and the mass-to-charge ratio, was performed using ABB Extrel's Merlin Automation Data System.

Quantification of Alkalichlorides by HPMS. The complex properties of the free-jet expansion inside the first stage of a HPMS system have led to some difficulties in the quantification of the different gas species.²⁷ Therefore, HPMS systems have most often been used for qualitative analysis or semiquantitative analysis. For a reliable quantification, the

total concentration of gas species to be measured must be kept very low, in relation to the carrier gas in which they are diluted. Otherwise, several separation phenomena may occur.²⁵

In case of the sorption experiments presented in this study, the carrier gas consisted of a constant mixture of $\text{He}/\text{H}_2/\text{H}_2\text{O}$. The amounts of alkali chlorides (NaCl and KCl) in the range of 0–100 ppmv did not significantly change the properties of the free-jet expansion and could easily be quantified. The quantification was achieved by calibrating the HPMS system before the experiments. Alkali chlorides were the only alkali species detected in the experiments. The alkali chloride concentration (NaCl and KCl) in the gas stream was determined using eqs 1 and 2.

$$C_{\text{NaCl}} = \frac{1}{K_{\text{NaCl}}} \left([I(\text{NaCl}^+)] + [I(\text{Na}^+)] + 2 \left\{ [I(\text{Na}_2\text{Cl}^+)] \frac{\sigma(\text{NaCl})}{\sigma(\text{NaCl}_2)} \right\} \right) \quad (1)$$

$$C_{\text{KCl}} = \frac{1}{K_{\text{KCl}}} \left([I(\text{KCl}^+)] + [I(\text{K}^+)] + 2 \left\{ [I(\text{K}_2\text{Cl}^+)] \frac{\sigma(\text{KCl})}{\sigma(\text{KCl}_2)} \right\} \right) \quad (2)$$

Here, $I(i^+)$ is the intensity of ion i^+ , corrected for isotopic distribution, and $\sigma(j)$ is the ionization cross section of gaseous species j . The ions NaCl^+ and KCl^+ originate from simple ionization of the gaseous species NaCl and KCl . The ions Na_2Cl^+ [$(\text{NaCl})_2(g)$], K_2Cl^+ [$(\text{KCl})_2(g)$], Na^+ [$\text{NaCl}(g)$], and K^+ [$\text{KCl}(g)$] originate from the gaseous species given in brackets, via fragmentation (see Hilpert²⁸). The cross section ratios $\sigma(\text{NaCl})/\sigma(\text{NaCl}_2)$ and $\sigma(\text{KCl})/\sigma(\text{KCl}_2)$ were taken as 0.66 following the general assumption that the ionization cross section of a molecule is smaller than the value predicted by the additivity rule (see, e.g., Drowart and Goldfinger²⁹).

The calibration factor K_{NaCl} (arb. units/ppmv) was determined using special calibration runs. In these runs, the furnace was heated and as soon as the desired temperature was attained, the NaCl source was inserted into the tube and the carrier gas flow (same composition as that for the sorption experiments) was turned on. After 50 h, the source was removed. The alkali loss of the source was then determined by comparing the weight of the source before and after the experiment. Considering the total gas volume flow during the 50 h, the total NaCl concentration in the gas phase was calculated and K_{NaCl} was determined. K_{KCl} was determined in the same way in separate runs. Because of the different fragmentation of NaCl and KCl and the different ionization cross sections of both molecules and fragments, the values for K_{NaCl} and K_{KCl} differed by a factor of 2.

To sample the gas stream, the HPMS system and the furnace were connected as shown in Figure 2 for a maximum duration of 5 min, to prevent corrosion of the stainless-steel sampling cone. For the first 2 min, the cone was exposed to the hot gas, to heat the tip, and then the gas was sampled for 1 min and the signal was averaged. According to the mass spectra recorded every 5 h over the course of the 50 h time period of the calibration, the source was providing a constant NaCl concentration in the gas stream (relative uncertainty of $\pm 5\%$). The calibration runs with NaCl concentrations of 2, 5, and 10 ppmv showed a linear correlation between these values and the concentration determined via HPMS by measuring the ion intensities of Na^+ , NaCl^+ , and Na_2Cl^+ and using eq 1. The total uncertainty for the quantification of NaCl with the HPMS system calibrated in the manner described previously is estimated to be $<10\%$ in the ppmv range and $<30\%$ for a

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Table 1. Chemical and Phase Analysis of Tested Sorbents before the Experiments

sorption material	Composition								main phases present
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	CaO	MgO	
Weipa bauxite	56.9	4.75	5.42	2.39	0.01	0.02			AlO(OH), Al ₂ Si ₂ O ₅ (OH) ₄ , Al(OH) ₃ , SiO ₂ , Fe ₂ O ₃
mullite M72	64.64	28.25	0.19	0.17	<0.01	0.36	0.05	0.04	Al ₆ Si ₂ O ₁₃ (mullite)
mullite MU60	58.4	36.38	1.03	2.59	0.04	0.08	0.05	0.06	Al ₆ Si ₂ O ₁₃ (mullite)
silica	<0.2	89.24	0.2	0.17	0.22	0.12	0.18	0.04	SiO ₂ (quartz, cristobalite, tridymite-M)
cat litter	13.42	50.72	4.29	0.74	1.49	1.08	2.94	3.49	Al ₂ Si ₄ O ₁₀ , SiO ₂

Table 2. Chemical and Phase Analysis of the Sorbents after the Experiments

sorption material	size ^a (mm)	duration (h)	gas composition (%)	Na (mass %)	K (mass %)	Cl (mass %)	main phases present
Na-sorption Experiments (85 ppmv NaCl)							
Weipa bauxite	3–4	52	He/H ₂ /H ₂ O (94/3/3)	5.4	<0.02	0.735	NaAlSiO ₄ , Al ₂ O ₃
	4–5	52	He/H ₂ /H ₂ O (94/3/3)	5.4	<0.02		n.i. ^b
	1.5–3	192	He/H ₂ /H ₂ O (94/3/3)	7.7	<0.02	0.423	NaAlSiO ₄ , Al ₂ O ₃ , NaAlO ₂
	1.5–3	52	He/H ₂ (97/3)	2.8	0.14	1.027	n.i. ^b
mullite M72	1.5–3	52	He/H ₂ /H ₂ O (94/3/3)	0.48	0.15		Mullite, NaAlSiO ₄ (nepheline)
mullite MU60	1.5–3	52	He/H ₂ /H ₂ O (94/3/3)	0.5	0.056		Mullite, NaAlSiO ₄ (nepheline)
silica	2	52	He/H ₂ /H ₂ O (94/3/3)	3.0	<0.02	0.113	n.i. ^b
cat litter	1.5–3	52	He/H ₂ /H ₂ O (94/3/3)	5.9	0.54	0.01	NaAlSiO ₄ , NaAlSi ₃ O ₈
	1.5–3	192	He/H ₂ /H ₂ O (94/3/3)	11.4	<0.02	0.011	NaAlSiO ₄ , NaAlSi ₃ O ₈
	1.5–3	52	He/H ₂ (97/3)	4.4	0.4	0.131	NaAlSiO ₄ , NaAlSi ₃ O ₈
K-sorption Experiments (80 ppmv KCl)							
Weipa bauxite	1.5–3	52	He/H ₂ /H ₂ O (94/3/3)	0.055	4.4	0.318	n.i. ^b
	1.5–3	192	He/H ₂ /H ₂ O (94/3/3)	<0.01	6.2	0.425	KAlSiO ₄ , Al ₂ O ₃
cat litter	1.5–3	52	He/H ₂ /H ₂ O (94/3/3)	<0.01	9.0	0.008	KAlSi ₃ O ₄ , KAlSiO ₄
	1.5–3	192	He/H ₂ /H ₂ O (94/3/3)	<0.01	11.0	0.011	KAlSi ₃ O ₄ , KAlSiO ₄

^a Diameter. ^b Not identified.

NaCl concentration of 50–100 ppbv. The total uncertainty for KCl quantification was the same as that for the NaCl quantification.

Investigated Sorbents and Post-Experiment Analysis. Five different sorbents have been tested (Table 1). Activated bauxite has been tested and characterized by other authors previously and observed to be a suitable sorbent for alkalis under oxidizing atmospheres. Two types of mullite have been chosen, because of their high ratio of SiO₂/Al₂O₃. Silica was used to test the influence of alkali on pure SiO₂. The fifth sorbent presented was bentonite and, as detailed analysis has revealed, is similar to previous tested sorbents such as emathlite or Fuller's earth, because of its high CaO content and high porosity. Bentonite was purchased as cat litter in a supermarket in Germany. Table 1 shows the chemical composition and the main crystalline phases of the tested sorbents before the experiments. All sorbents were heat-treated for 10 h at 750 °C in a reducing atmosphere, to provide the same initial conditions. The materials were characterized using scanning electron microscopy/energy-dispersive X-ray (SEM/EDX) and X-ray diffraction (XRD) analyses before and after the experiments.

Results

All the sorbent testing presented in this paper was conducted using the flow channel reactor setup (see Figure 2). Two types of experiments were performed. First, several packed-bed experiments with a short sorbent bed and high alkali load of the gas stream were conducted, to gain information on the maximum load capacity of the tested sorbents. During these screening tests, general information, such as the influence of water on the alkali uptake and the sorption mechanism, was obtained. Second, packed-bed studies with low alkali content in the carrier gas and long sorbent beds were conducted, to determine the maximum capability of gas cleaning.

Screening Experiments. For the screening experiments, the inner diameter of the reactor tube was 20

mm, and the length of the sorbent bed was 12 mm. The total sorbent bed volume was 3.77 cm³, which led to a short duration of the experiments. A total gas flow of 3 L/min (at standard temperature and pressure, STP) at a gas temperature of 750 °C was used, resulting in a very short space time for the sorbent bed of 0.02 s. In addition, an almost-constant alkali load over the sorbent bed length was obtained, which led to easier evaluation of the post-experiment chemical analysis. The duration of the experiments was 52 and 192 h. For better comparison, all sorbent particles were sized to be 1.5 and 3 mm in diameter. Either solid NaCl or KCl was used as an alkali source. The alkali concentration in the gas stream was set to 85 ppmv NaCl for Na-sorption experiments and 80 ppmv KCl for K-sorption experiments. The results of the screening experiments are summarized in Table 2.

These preliminary experiments revealed that, after 52 h, the highest uptake for sodium was reached by activated bauxite (54 mg/g) and bentonite (59 mg/g). In the case of bentonite, most of the initially bound potassium in the sorbent was released during the experiment.

Both mullites showed the lowest sorption capacities (4.8 and 5.0 mg/g), because of their high density. The value for silica was 30 mg/g. The formation of a glassy layer of sodium silicate with a sodium content up to 150 mg/g on the surface of the particles probably inhibited further alkali uptake. Because of their high sorption potential, only bauxite and bentonite were selected for further investigations.

A second set of experiments was conducted for a duration of 192 h (see Table 2). The total amount of sodium absorbed was 77 mg/g for bauxite and 114 mg/g for bentonite. In bentonite, no potassium could be found in the sorbent after the tests. Almost no chlorine could

Table 3. Alkali Concentrations Measured Downstream of Different Sorbent Beds

sorption material	size ^a (mm)	duration (h)	bed length (mm)	tube size ^b (mm)	gas composition (%)/4 L/min	lowest alkali concentration measured downstream of bed	concentration at the end of the experiment
HPMS–Na-sorption Experiments (65 ppmv NaCl)							
Weipa bauxite	3	77	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	80 ppbv	13.7 ppmv
	3	77	20	25	He/H ₂ /H ₂ O (94/3/3 vol %)	320 ppbv	34 ppmv
	3	97	100	25	He/H ₂ /H ₂ O (94/3/3 vol %)	90 ppbv	5 ppmv
	3	10	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	90 ppbv	
					+ 1500 ppmv SO ₂		
mullite M72	3–4	7	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	4.8 ppmv	14.3 ppmv
	3–4	7	50	25	He/H ₂ (97/3 vol %)	45 ppmv	60 ppmv
cat litter	3	79	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	40 ppbv	13.4 ppmv
HPMS–K-sorption Experiments (60 ppmv KCl)							
Weipa bauxite	3	32	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	80 ppbv	11 ppmv
		69	100	25	He/H ₂ /H ₂ O (94/3/3 vol %)	65 ppbv	10 ppmv
cat litter	3	54	50	25	He/H ₂ /H ₂ O (94/3/3 vol %)	40 ppbv	7 ppmv

^a Diameter. ^b Inner diameter of tube.

be found in these samples either, whereas the bauxite samples had a chlorine content of up to 1 wt %.

XRD analysis revealed nepheline (NaAlSi₃O₈) as the main alkali phase in both sorbents. In addition to that, especially in the 192 h experiment in bauxite samples that contained high Al₂O₃ concentrations, NaAlO₂ was formed. In bentonite, albite (NaAlSi₃O₈) was the predominant alkali phase. Performing the same flow channel experiment for 52 h in a dry atmosphere led to a reduction in sodium uptake for both bauxite (28 mg/g) and bentonite (44 mg/g).

After the Na sorption experiments, bauxite and bentonite were tested, in regard to their capability to absorb potassium. For bauxite, the total amount of potassium absorbed was significantly lower after 52 h (44 mg/g) and 192 h (62 mg/g), compared to the amount of sodium absorbed in the Na-sorption experiments. Although bentonite showed a very high potassium uptake after 52 h, the total amount of potassium absorbed after 192 h was in the same range as that observed in the Na-sorption experiments (110 mg/g), on a weight basis. The chemical analysis showed that no sodium was left in the bentonite after the tests; therefore, all of the sodium must have been substituted or released during the potassium uptake. A maximum concentration of 200 (150) mg/g sodium (potassium) on the surface of the bentonite sorbent particles was determined after the 192 h experiment.

During the screening experiments with NaCl, the flow channel reactor was coupled with the HPMS occasionally, to obtain information on the gas composition and draw conclusions concerning the chemical reactions inside the sorbent bed. Figure 4 shows the ions of the species involved in the alkali uptake reaction and their intensities during the experiment, using silica as a sorbent. Relative to the uptake, only HCl⁺, NaCl⁺, and Na₂Cl⁺ ((NaCl)₂ fragment) ions could be found in the spectra. The same behavior was observed for all other tested sorbents. In experiments with no water in the carrier gas, the formation of HCl inside the sorbent bed was significantly reduced and more NaCl passed through the bed.

Extensive Sorption Studies on Selected Materials. A tube (diameter of 25 mm) larger than in the screening experiments was used in the extensive sorption studies, to increase the amount of sorbent in the tube. The length of the sorbent bed was increased to 50 mm, which led to a total bed volume of 24.5 cm³. Using

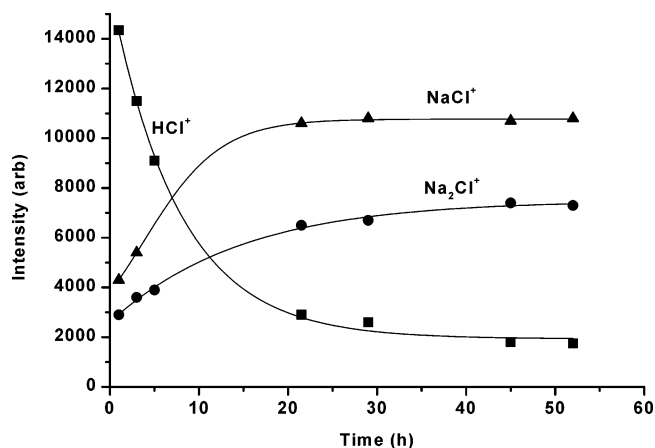


Figure 4. Intensity of ions of involved species during sorption experiments versus time measured downstream of a sorbent bed of silica. Carrier gas composition: 3 L/min He/H₂/H₂O (94/3/3 (vol %)), 85 ppmv NaCl.

the same He/H₂/H₂O gas mixture as that in the screening experiments, the gas flow was set to 4 L/min (STP). The residence time of the gas in the sorbent bed was 0.1 s. The source delivered a constant NaCl load of 65 ppmv into the gas stream. The HPMS system was calibrated for NaCl quantification, as described in the Experimental Section. The overall NaCl content of the gas stream exiting the reactor was determined by connecting the HPMS to the flow channel reactor. The results of the HPMS experiments are shown in Table 3.

Quantification of NaCl downstream of the sorbent bed, versus time, was performed for activated bauxite, bentonite, and mullite (Figure 5). The experiments clearly show that the capability of mullite to remove NaCl from the gas stream successfully is low. Five hours after the beginning of the experiment, the total amount of NaCl detected with the HPMS was >10 ppmv, showing that mullite cannot be considered to be a suitable sorbent. In contrast to this, bauxite and bentonite were able to reduce the NaCl content of the gas to values of <100 ppbv. The measured values for bentonite (~40 ppbv) have a tendency to be slightly lower than those for bauxite (~80 ppbv). Bauxite and bentonite have also been investigated to determine their capability of removing potassium from the gas stream (Figure 6). Therefore, the solid NaCl source was replaced by solid KCl. All other parameters were kept the same as those in the Na-sorption experiments (see Table

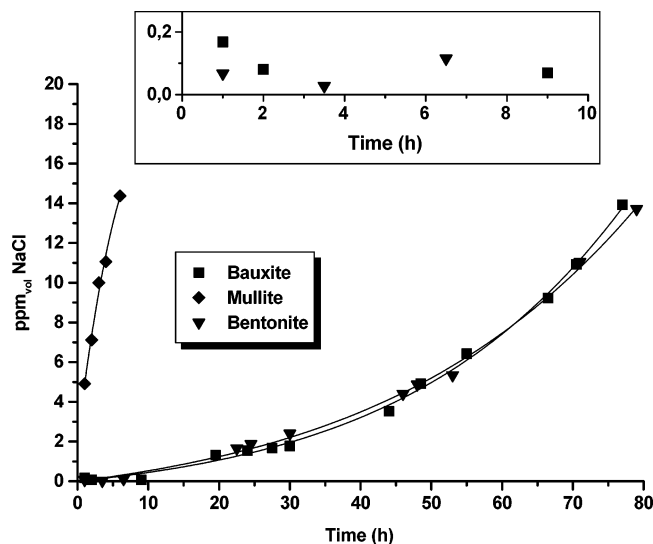


Figure 5. NaCl concentration versus time downstream of the sorbent bed for different sorbents. Carrier gas composition: 4 L/min He/H₂/H₂O (94/3/3 (vol %)), 65 ppmv NaCl.

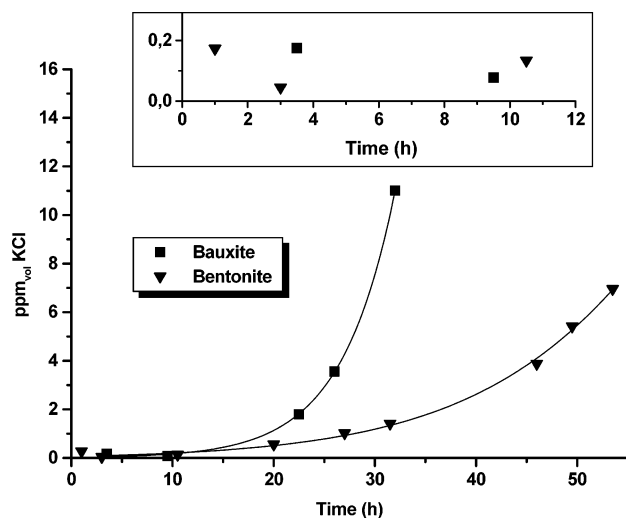


Figure 6. KCl concentration versus time downstream of the sorbent bed for different sorbents. Carrier gas composition: 4 L/min He/H₂/H₂O (94/3/3 (vol %)), 60 ppmv KCl.

3). Both sorbents were able to reduce the KCl content of the gas stream to values of <100 ppbv.

To investigate the influence of sulfur on the sorption process, one additional experiment was performed, using bauxite as the sorbent. A carrier gas stream of 4 L/min (STP) He/H₂/H₂O and a NaCl concentration of 1500 ppmv was adjusted. After 1 h of the experiment, 1500 ppmv SO₂ were added to the carrier gas and the mass spectra were monitored via HPMS. As expected, almost all of the SO₂ reacted with the H₂ in the carrier gas to form H₂S. The presence of SO₂ in the carrier gas had no influence on the potential of the sorbent to reduce the alkali concentration in the gas stream.

The influence of the sorbent bed length on the NaCl-removing capability of bauxite was investigated (Figure 7) via HPMS, by varying the length of the sorbent bed from 20 mm to 100 mm and measuring the NaCl content of the gas stream exiting the flow channel reactor by HPMS. The measured values for a bed length of 20 mm amounted to 320 ppbv, indicating that the contact time between the gas and the sorbent was too low. On the

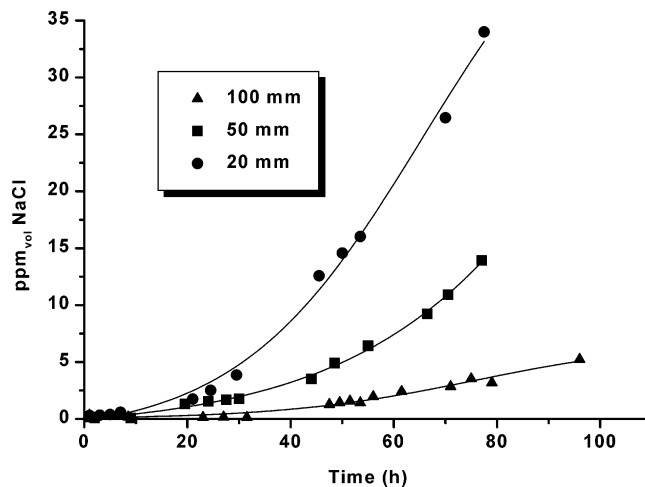


Figure 7. NaCl concentration versus time downstream of a sorbent bed of bauxite for different bed lengths. Carrier gas composition: 4 L/min He/H₂/H₂O (94/3/3 (vol %)), 60 ppmv KCl.

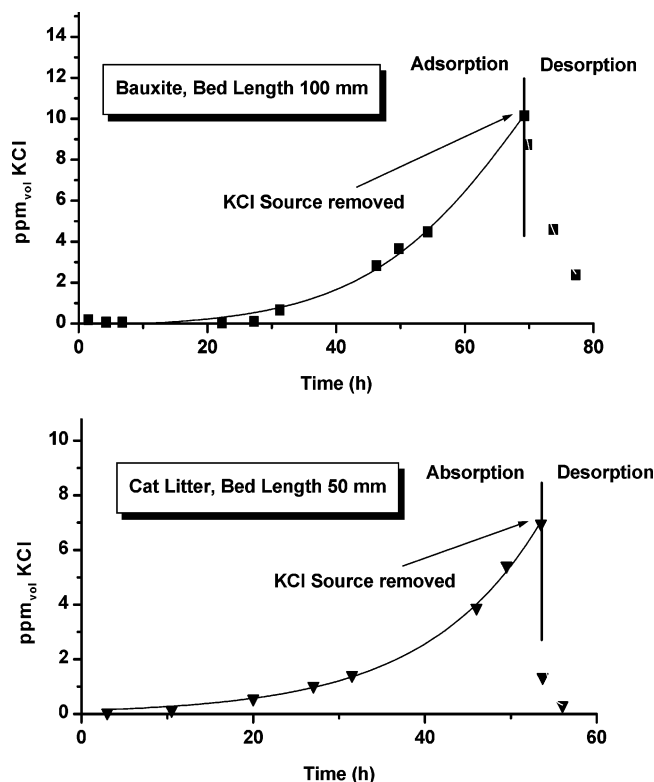


Figure 8. Alkali uptake and release from sorbent beds of bauxite and bentonite (cat litter) investigated before and after removing the KCl source from the carrier gas.

other hand, increasing the bed length to >50 mm did not reduce the alkali content of the gas stream significantly further.

For investigation of the reversibility of the sorption process, at the end of the K-sorption experiments, the KCl source was removed from the reactor and the carrier gas was kept flowing. The composition of the gas stream leaving the sorbent bed was monitored by HPMS. In the case of bauxite, the KCl signal remained on the same level for 5 min after the source was removed, and then it slowly decreased (Figure 8). For bentonite, removal of the source led to an immediate decrease in the KCl signal, to ~20% of the level before the source was removed. This behavior is closely related

Table 4. Alkali Vapor Pressures over Different Alkali Aluminosilicates under Experimental and Power-Plant Conditions

alkali phase	Conditions	
	experimental ^a	power plant ^b
NaCl concentration (ppmv)		
NaAlSi ₃ O ₈ (albite)	0.0467	0.04365
NaAlSiO ₄ (nepheline)	0.630	0.602
NaAlO ₂	25.7	10.7
KCl concentration (ppmv)		
KAlSi ₃ O ₈ (microcline)	0.0467	0.0148
KAlSi ₂ O ₆	0.478	0.154
KAlSiO ₄	18	7
KAlO ₂	47	22

^a He/3% H₂O/3% H₂/60 ppmv HCl, 1 bar, 750 °C. ^b 60% N₂/12.5% CO₂/11.5% CO/10% H₂O/5.97% H₂/0.03% HCl, 10 bar, 750 °C.

to the amount of chlorine determined in the sorbents by chemical analysis after the experiments (see Table 2).

Thermodynamic Computations. Thermodynamic computations based on the FactSage program and the Fact database were used to determine the vapor pressures of sodium and potassium over several alkali aluminosilicate phases. These computations were performed for two different reasons. On one hand, the computed values could be compared with the results of the laboratory HPMS experiments. On the other hand, computations of the partial pressures of sodium and potassium in equilibrium with these phases in a simulated flue gas can be used to estimate the alkali concentration after the sorbent bed in a future power plant. The results of these calculations are shown in Table 4.

Discussion

Screening Experiments. After 192 h, bentonite showed the highest alkali uptake, with 114 mg/g of sodium and 110 mg/g of potassium, respectively. Maximum concentrations of 200 mg/g of sodium and 150 mg/g of potassium at the sorbent surface showed that the maximum sorption capacity of bentonite was not attained after 192 h. The formation of albite (NaAlSi₃O₈) and nepheline (NaAlSiO₄) in the Na-sorption experiments and the formation of microcline (KAlSi₃O₈) and kalsilite (KAlSiO₄) in the K-sorption experiments as the main alkali phases revealed the chemical bonding of sodium and potassium in the sorbent lattice. This result reveals a significant reduction in alkali uptake under dry conditions (see Table 2). Determination of the alkali phases formed in the K-sorption experiments was difficult for bentonite, because of the existence of large amorphous areas. Bentonite seems to be a highly suitable sorbent for alkali reduction under reducing conditions. The high content of silica leads to a high sorption capacity for alkalis by chemical bonding; small amounts of Al₂O₃, on the other hand, stabilize the matrix and provide a high enduring porosity in the material. No potassium could be detected after the Na-sorption experiments and no sodium could be detected after the K-sorption experiments. This can be explained by equilibration which, at high alkali levels in the gas phase, leads to a substitution of naturally bound alkalis in the sorbent by alkalis from the surrounding atmosphere.

The question about the type of sorption mechanism that prevails in bauxite, either chemical sorption or physical sorption,⁶ has led to great confusion in earlier research. A detailed analysis of bauxite particles after the sorption experiments shows that the reason for this may be found in the inhomogeneity in chemical composition of different particles. Bauxite particles with a high silica content have a tendency to chemically bind sodium and potassium in silica-rich phases such as NaAlSiO₄ and KAlSiO₄, whereas in bauxite particles with a high Al₂O₃ content, most of the alkalis are bound as NaAlO₂. The formation of the latter phase seems to be favored in long-term experiments. However, the high content of chlorine that is observed in bauxite (via chemical analysis) may indicate that a fraction of the sodium and potassium is absorbed physically. The maximum sorption capacity of bauxite after 192 h—77 mg/g for sodium and 62 mg/g for potassium—was significantly lower than the capacity of bentonite.

Extensive Sorption Studies on Selected Materials. HPMS experiments, as depicted in Figure 2, were conducted to obtain information on the sorption potential of bentonite and bauxite for sodium and potassium, to determine the influence of sorbent bed length and carrier gas SO₂ concentration and to predict the alkali release from an alkali-laden sorbent. For all experiments, a standard gas mixture of He/H₂O/H₂ was used. Concentrations of 65 ppmv NaCl or 60 ppmv KCl were adjusted in the standard gas mixture as contaminants.

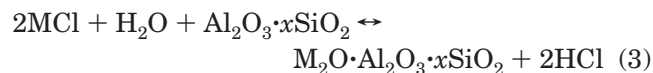
The HPMS experiments revealed a possible reduction of the NaCl concentration in the carrier gas to 80 ppbv for bauxite and 40 ppbv for bentonite. The high potential of these two sorbents to reduce the alkali content in the gas is mainly due to their high porosity, which leads to high diffusion rates into the sorbent core. XRD analysis of the sorbent after the experiment revealed that the formation of NaAlSi₃O₈ was responsible for the good performance of these sorbents during the first 10 h of the experiment (see Figure 5). After 15 h, the formation of NaAlSiO₄ becomes dominant. The beginning of the formation of this phase is the reason for the increase of the gas-phase NaCl for bauxite and bentonite. This increase is in close agreement with the alkali partial pressures over NaAlSi₃O₈ and NaAlSiO₄, as obtained from the thermodynamic computations (see Table 4). The sodium partial pressures over NaAlSi₃O₈ and NaAlSiO₄ are comparable for both the experiment and thermodynamic computations.

Further experiments showed that the KCl concentration can be reduced to values of 65 ppbv for bauxite and 40 ppbv for bentonite, under these conditions (see Figure 6). Therefore, the potential of bauxite and bentonite to reduce the level of contamination must be considered to be approximately the same for KCl and NaCl. In case of the K-sorption, the formation of KAlSi₃O₈ is responsible for the low potassium concentration in the gas phase (see Table 6). Tracing the sodium and potassium concentrations in the gas, relative to time, a much higher increase of the alkali concentration downstream of a bed of bauxite can be observed than that downstream of a bed of bentonite (see Figures 5 and 6). This result corresponds directly to the different sorption capacities for sodium and potassium determined by the screening experiments (see Table 2) and is mainly

caused by the higher SiO₂ content of bentonite. In contrast to the Na-sorption experiments (see Figure 5), in the K-sorption experiments (see Figure 6), the alkali concentration, relative to time in the gas phase for bauxite, increased much faster. The reason for that phenomenon can be found in the higher molecular weight of K atoms, in comparison to Na atoms. The change in weight for the samples in both experiments might be the same, which leads to a smaller number of K atoms being bound in the sorbent lattice and ultimately results in a higher level of alkalis in the carrier gas.

Unlike earlier experiments under oxidizing atmospheres that showed a strong influence of sulfur on the sorption behavior, under reducing atmospheres, no influence of sulfur on the alkali concentration downstream of the sorbent bed could be measured. The lack of oxygen leads to the formation of hydrogen sulfide (H₂S), which does not further react with the alkalis in the gas.

HPMS experiments that used a dry carrier gas of He/H₂ showed a strong influence of water on the sorption process. Especially using bentonite, the absence of water led to an almost complete flow of the alkali chlorides through the sorbent bed without participating in any reaction. The results of these measurements, which are in close agreement with the results of the screening experiments (see Table 2), underline the validity of eq 3.



This reaction, which describes the formation of alkali aluminosilicates via a chemical sorption process, has been predicted by other authors.^{4,18} However, using the HPMS technology, this is the first time that eq 3 can be validated via on-line measurements.

Experiments on the influence of sorbent bed length on NaCl removal, using bauxite as a sorbent, showed that after a certain critical length is exceeded, further increases in the sorbent bed length do not lead to further reductions in the alkali concentration in the gas. This can be explained by the equilibration of the alkalis in the gas after a certain time period in the sorbent bed, which corresponds to a certain bed length. Further increases in the bed length become useless. In the case of bauxite, for both NaCl and KCl, this critical value, under the experiment conditions, was ~50 mm. Reducing the bed length to 20 mm led to much-higher alkali levels. Equilibration was not completed at this short bed length. However, considering the very low space time in the sorbent bed (only 0.1 s), the kinetics of sodium and potassium absorption by these sorbents is very fast.

After the KCl source was removed from the flow channel in the flow channel experiments, in the case of bauxite, the KCl signal remained on a constant level for several minutes (see Figure 8). Because there is no other possible way for chlorine to be bound in bauxite, the measured KCl probably originates from the release of potassium physically absorbed as a chloride. This observation is in close agreement to the results of the annealing experiments (see Table 2). Therefore, the alkali uptake of bauxite must be viewed as being partly reversible in a technical sense. In the case of bentonite,

all of the potassium is chemically bound. The thermodynamic calculations show that the partial pressures of alkali hydroxides over aluminosilicates are lower than the partial pressures of alkali chlorides, by a factor of 100, and, under the given conditions, the absorption of sodium and potassium on bentonite can be considered to be irreversible, in a technical sense.

Estimation of the Amount of Sorbent Needed for a Second-Generation Pressurized Fluidized-Bed Combustion Power Plant. As the experiments show, using bentonite as a sorbent can reduce the alkali concentration in the gas stream to values of ~40 ppbv for sodium and potassium, under the experimental conditions. These values are in close agreement with the concentrations of sodium and potassium over aluminosilicates (albite, microcline), as calculated from the Fact database. Similar calculations for a simulated flue gas atmosphere show a similar potential of bentonite to reduce the alkali concentration under power plant conditions (see Table 4). Further calculations were performed, using a reactor model and the Fact database, to estimate the alkali concentration after the combustor at the entrance to the gas turbine. All relevant parameters used in these calculations can be taken from Figure 1. The value for the alkali concentration at the entrance to the gas turbine is then calculated to be 25 ppbv. The alkali reduction to this low value is promoted by mixing the flue gas with secondary air before the gas turbine (see Figure 1). This value is on the order of the maximum concentration demanded by the gas turbine manufacturers.

For the given power plant, a total alkali concentration of ~3 mg/g (STP) at 700 °C or 9 mg/g (STP) at 800 °C after the gasifier and ash removal can be expected, as the thermodynamic calculations reveal. For a 500 MW_{el} power plant, the volume flow of the flue gas at that point is estimated to be 80 m³/s (10 bar) at a gasification temperature of 700 °C and ~88 m³/s (10 bar) at a gasification temperature of 800 °C. This results in a total alkali mass flow of ~9 kg/h at 700 °C or 28.5 kg/h at 800 °C, respectively. Assuming a maximum load capacity for bentonite of 9 wt %, a total absorption volume of 4.9 m³ will be needed at 700 °C for a residence time of the sorbent of 50 h. The total sorbent consumption under these conditions will be 98 kg/h. At a gasifier temperature of 800 °C, the total consumption will increase to 316 kg/h, which leads to a needed sorption volume of 15.8 m³.

Conclusions

The sorption of alkali metals under reducing conditions has been the focus of attention, because of the role of alkali metals in hot corrosion in modern second-generation pressurized fluidized-bed combustion (2nd-Gen PFBC) systems. In laboratory-scale flow channel experiments at 750 °C, bentonite and bauxite have shown the best ability to remove alkalis from the gas phase. With bentonite, the total NaCl and KCl concentration in the hot gas can be reduced to values of <50 ppbv under laboratory conditions. Thermodynamic calculations show that, in the power plant, values as low as 25 ppbv can be expected using this sorbent. In the case of bentonite, chemical sorption prevails, and, therefore, the sorption process is irreversible in a

technical sense. In bauxite, alkalis are bound in both forms (chemically and physically) in the form of chlorides. Therefore, the sorption process for bauxite is partly reversible.

All the gas analysis downstream of the sorbent bed has been performed using high-pressure mass spectrometry (HPMS). HPMS is the only method that can deliver both qualitative and quantitative analyses of hot gases at the same time. Therefore, not only could the alkali concentrations in the hot gas be determined, but also conclusions could be drawn concerning the chemical reactions that occur inside the sorbent bed, depending on the gas composition.

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